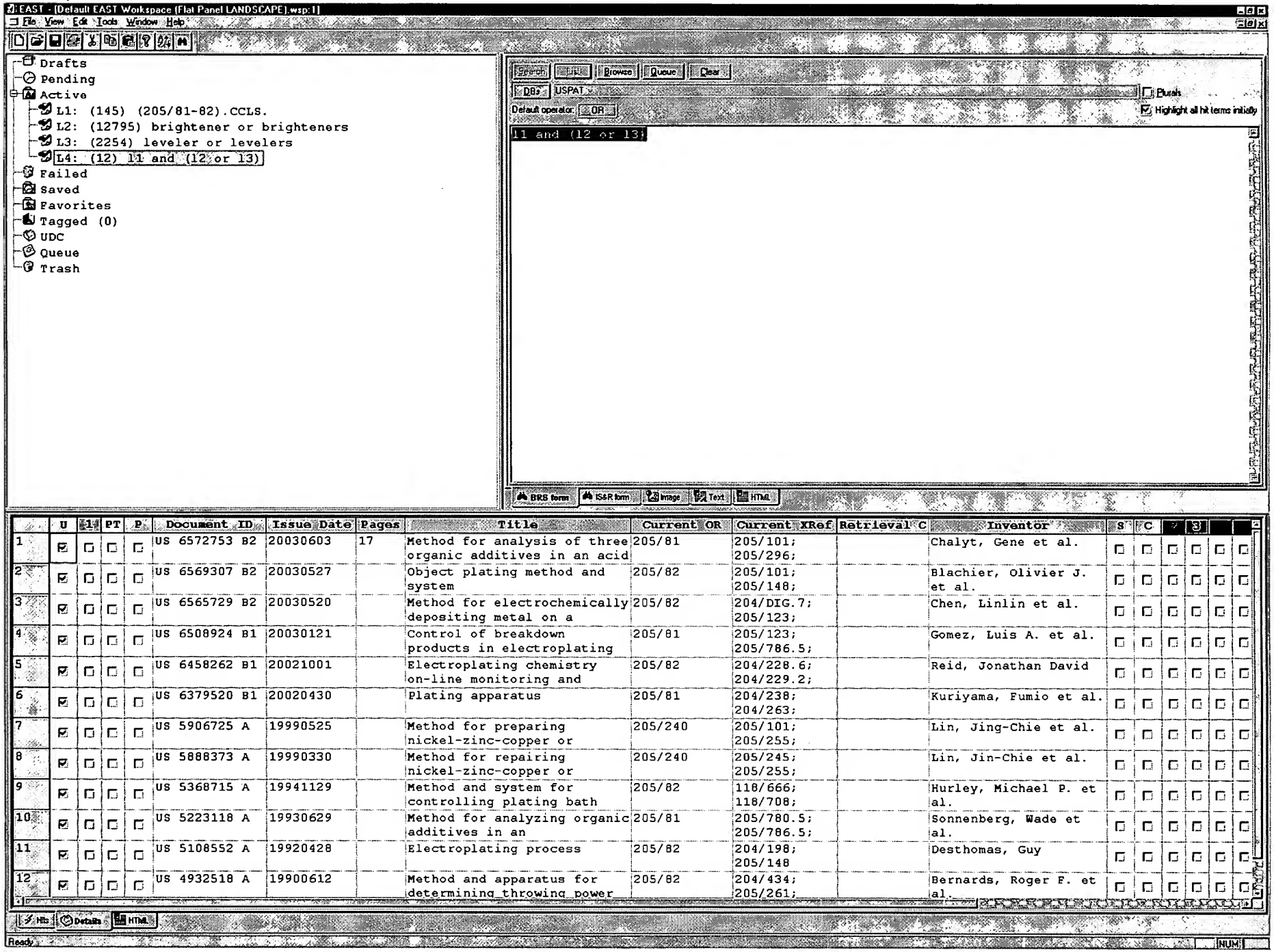

	U	L1	PT	P	Document ID	Issue Date	Pages	Title	Current OR	Current XRef	Retrieval C	Inventor	S	C	2	3		
1	☑	☐	☐	☐	US 6572753 B2	20030603	17	Method for analysis of three organic additives in an acid	205/81	205/101; 205/296;		Chalyt, Gene et al.	☐	☐	☐	☐	☐	☐
2	☑	☐	☐	☐	US 6569307 B2	20030527		Object plating method and system	205/82	205/101; 205/148;		Blachier, Olivier J. et al.	☐	☐	☐	☐	☐	☐
3	☑	☐	☐	☐	US 6565729 B2	20030520		Method for electrochemically depositing metal on a	205/82	204/DIG.7; 205/123;		Chen, Linlin et al.	☐	☐	☐	☐	☐	☐
4	☑	☐	☐	☐	US 6508924 B1	20030121		Control of breakdown products in electroplating	205/81	205/123; 205/786.5;		Gomez, Luis A. et al.	☐	☐	☐	☐	☐	☐
5	☑	☐	☐	☐	US 6458262 B1	20021001		Electroplating chemistry on-line monitoring and	205/82	204/228.6; 204/229.2;		Reid, Jonathan David	☐	☐	☐	☐	☐	☐
6	☑	☐	☐	☐	US 6379520 B1	20020430		Plating apparatus	205/81	204/238; 204/263;		Kuriyama, Fumio et al.	☐	☐	☐	☐	☐	☐
7	☑	☐	☐	☐	US 5906725 A	19990525		Method for preparing nickel-zinc-copper or	205/240	205/101; 205/255;		Lin, Jing-Chie et al.	☐	☐	☐	☐	☐	☐
8	☑	☐	☐	☐	US 5888373 A	19990330		Method for repairing nickel-zinc-copper or	205/240	205/245; 205/255;		Lin, Jin-Chie et al.	☐	☐	☐	☐	☐	☐
9	☑	☐	☐	☐	US 5368715 A	19941129		Method and system for controlling plating bath	205/82	118/666; 118/708;		Hurley, Michael P. et al.	☐	☐	☐	☐	☐	☐
10	☑	☐	☐	☐	US 5223118 A	19930629		Method for analyzing organic additives in an	205/81	205/780.5; 205/786.5;		Sonnenberg, Wade et al.	☐	☐	☐	☐	☐	☐
11	☑	☐	☐	☐	US 5108552 A	19920428		Electroplating process	205/82	204/198; 205/148		Desthomas, Guy	☐	☐	☐	☐	☐	☐
12	☑	☐	☐	☐	US 4932518 A	19900612		Method and apparatus for determining throwing power	205/82	204/434; 205/261;		Bernards, Roger F. et al.	☐	☐	☐	☐	☐	☐

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3	US 6565729 B2	53							☑				USPAT
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5	US 6458262 B1	13						☑					USPAT
6	US 6379520 B1	21						☑					USPAT
7	US 5906725 A	6						☑					USPAT

US-PAT-NO: 6508924

DOCUMENT-IDENTIFIER: US 6508924 B1

TITLE: Control of breakdown products in electroplating baths

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Brief Summary Text - BSTX (3):

Electroplating is a complex process involving multiple ingredient, in a plating bath. It is important that the concentration of several of the ingredients be kept with in close tolerances in order to obtain a high quality deposit. In some cases, chemical analysis of individual solution constituents can be made regularly (such as pH measurement for acid con tent), and additions made as required. However, other addition agents such as brighteners, leveling agents, suppressants, etc., together with impurities, cannot be individually analyzed on an economical or timely basis by a commercial plating shop. Their operating concentration is low and their quantitative analysis is complicated and subject to error.

Brief Summary Text - BSTX (6):

The electroplating of through-hole interconnections in the manufacture of multilayer printed circuit boards is an example of the use of an electroplating metal where high quality plating is required. It is known that the concentration of the organic additives, such as brighteners and levelers, within the plating solution must be maintained in low concentration (typically less than 100 parts per million parts of solution--ppm) in order to obtain acceptable deposits on printed circuit boards. This must be done to maintain proper mechanical properties for resistance to thermal stresses encountered during manufacture and use and to assure the proper thickness of the deposit in the through-holes and leveling. The concentration of the organic additive agents fluctuates because of oxidation at the anode. Reduction at the cathode, and chemical degradation. When the additive level is insufficient, deposits are burned and powdery in appearance whereas excessive addition agents induce brittleness and non-uniform deposition. Hull cell tests, Bone Pattern tests, and Pencil tests, combined with periodic additions of fresh additives, were the methods used to maintain a control concentration of the additive until recently. These methods were unreliable and circuit board quality suffered as a consequence of these unreliable methods.

Brief Summary Text - BSTX (8):

U.S. Pat. No. 5,223,118 (Sonnenberg et al.) discloses a method for determining the quantity of brighteners and levelers present in an electroplating bath for the plating of printed wiring board substrates. In this method, the determination of both brightener and leveler is accomplished in one step.

Detailed Description Text - DETX (4):

Many organic additives are used in metal electroplating baths, such as, but not limited to, leveling agents, brighteners, accelerators, suppressors, surfactants, wetting agents and the like. Certain organic additives are known to breakdown during the electroplating process to form breakdown products.

(12) **United States Patent**
Gomez et al.

(10) **Patent No.: US 6,508,924 B1**
(45) **Date of Patent: Jan. 21, 2003**

(54) **CONTROL OF BREAKDOWN PRODUCTS IN ELECTROPLATING BATHS**

(75) Inventors: **Luis A. Gomez**, Patchoque, NY (US); **Rozalia Beica**, Bayport, NY (US); **Denis Morrissey**, Huntington, NY (US); **Eugene N. Step**, Newton, MA (US)

(73) Assignee: **Shipley Company L.L.C.**, Marlborough, MA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 140 days.

(21) Appl. No.: **09/584,124**

(22) Filed: **May 31, 2000**

(51) Int. Cl.[7] **C25D 21/18**

(52) U.S. Cl. **205/81**; 205/82; 205/99; 205/123; 205/786.5; 205/787

(58) Field of Search 205/81, 82, 99, 205/123, 157, 786.5, 787

(56) **References Cited**

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4,089,754 A * 5/1978 Tremmel et al. ..... 204/43 T
4,132,605 A 1/1979 Tench et al.
4,917,774 A 4/1990 Fisher 204/153.1
5,223,118 A 6/1993 Sonnenberg et al. 205/81
5,252,196 A 10/1993 Sonnenberg et al. 205/296
5,935,402 A * 8/1999 Fanti 205/101
6,113,771 A * 9/2000 Landau et al. 205/123
6,224,737 B1 * 5/2001 Tsai et al. 205/123

FOREIGN PATENT DOCUMENTS

DE 199 11 447 A1 3/1999

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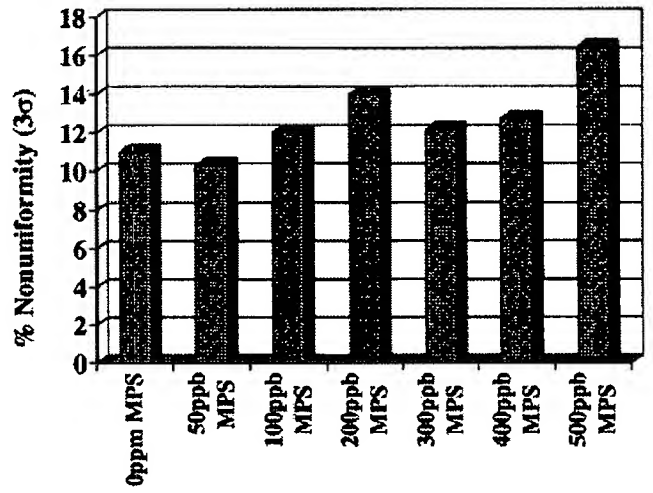
Primary Examiner—Nam Nguyen
Assistant Examiner—William T. Leader
(74) *Attorney, Agent, or Firm*—S. Mathew Cairns

(57) **ABSTRACT**

Disclosed are methods for analyzing additive breakdown products in electroplating baths as well as methods of controlling the presence of such breakdown products in electroplating baths.

11 Claims, 5 Drawing Sheets



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6	US 6379520 B1	21							☑				USPAT
7	US 5906725 A	6						☑					USPAT

US-PAT-NO: 6379520

DOCUMENT-IDENTIFIER: US 6379520 B1

TITLE: Plating apparatus

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Detailed Description Text - DETX (7):
With this construction, the power source 1-5 applies a predetermined voltage between the substrate 1-4 and anode 1-3, forcing metallic ions, such as Cu.sup.2+ to be emitted from the soluble anode 1-3 (for example, a phosphorous copper electrode). The metallic ions emitted from the anode 1-3 are deposited on the surface of the substrate 1-4 to form a metal plating film. After continuously performing the plating process and processing a plurality of substrate 1-4, the composition, concentration, and amount of the plating solution 1-1 varies. In response to these variations, additive solution 2-4 from the replenishing tank 2-2 and plating solution 2-5 from the replenishing tank 2-3 are supplied to the regulator tank 2-1 to maintain the composition and concentration of the plating solution 1-1 at predetermined values. The additive solution 2-4 in the replenishing tank 2-2 is an organic additive solution comprising a mixture of a polymer, leveler, carrier, and HCl.

Detailed Description Text - DETX (48):
With the construction described above, the power supply 11-5 applies a predetermined voltage across the substrate 11-4 and the anode 11-3, causing metallic ions such as Cu.sup.2+ to emit from the soluble anode 11-3 (which is a phosphorous copper electrode, for example) and deposit on the surface of the substrate 11-4 to form a metallic film. After continuous plating operations and after performing the process on a plurality of substrate S11-4, the composition and concentration of the plating solution 11-1, as well as the amount of the plating solution 11-1, fluctuates. Based on the state of these fluctuations, the regulating tank 12-1 is replenished with additive solution 12-7 or plating solution 12-8 from the replenishing tank 12-2 or replenishing tank 12-3, respectively, in order to maintain the composition and concentration of the plating solution 11-1 at predetermined values. The additive solution 12-7 contained in the replenishing tank 12-2 is an organic additive solution comprising a mixture of polymers, levelers, carriers, and HCl.

Claims Text - CLTX (13):
6. A plating apparatus according to claim 5, wherein said organic additive solution comprises a mixture of a polymer, a leveler, a carrier, and HCI.

Claims Text - CLTX (81):
42. A plating apparatus according to claim 41, wherein said organic additive solution comprises a mixture of a polymer, a leveler, a carrier, and HCI.

Current US Original Classification - CCOR (1):
205/81

(12) **United States Patent**
Kuriyama et al.

(10) **Patent No.: US 6,379,520 B1**
(45) **Date of Patent: Apr. 30, 2002**

(54) **PLATING APPARATUS**

(75) Inventors: **Fumio Kuriyama; Hiroyuki Ueyama; Junitsu Yamakawa; Kenichi Suzuki; Atsushi Chono, all of Tokyo (JP)**

(73) Assignee: **Ebara Corporation, Tokyo (JP)**

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/601,084**

(22) PCT Filed: **Nov. 26, 1999**

(86) PCT No.: **PCT/JP99/06600**

§ 371 Date: **Jul. 27, 2000**

§ 102(e) Date: **Jul. 27, 2000**

(87) PCT Pub. No.: **WO00/32850**

PCT Pub. Date: **Jun. 8, 2000**

(30) **Foreign Application Priority Data**

Nov. 30, 1998 (JP) 10-340576
Dec. 2, 1998 (JP) 10-342611

(51) **Int. Cl.**[7] **C25D 21/12**

(52) **U.S. Cl.** **205/81**; 204/238; 204/263; 204/269

(58) **Field of Search** 204/237, 252, 204/232, 263, 269, 238; 205/82, 81

(56) **References Cited**

U.S. PATENT DOCUMENTS

3,658,470 A * 4/1972 Zievers et al. 23/145

FOREIGN PATENT DOCUMENTS

JP 5-179496 7/1993
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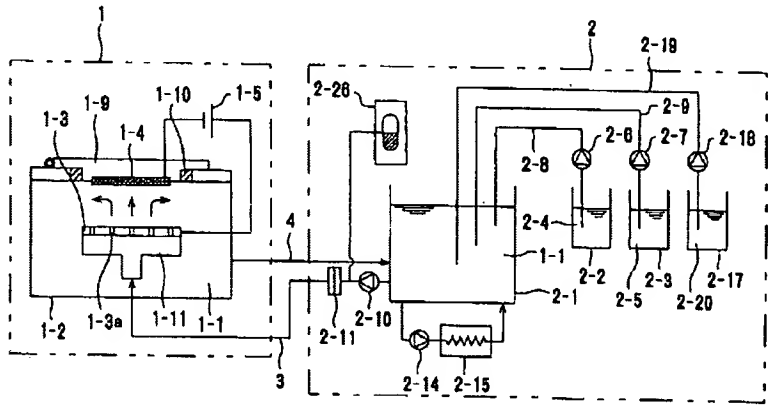
Primary Examiner—Donald R. Valentine
Assistant Examiner—Thomas H. Parsons
(74) *Attorney, Agent, or Firm*—Wenderoth, Lind & Ponack, L.L.P.

(57) **ABSTRACT**

The plating apparatus has a plating section in which a plating process is performed and a control section for regulating the plating solution. The plating section includes a plating bath containing plating solution, an anode provided in the plating solution, and a plating object serving as a cathode placed in the plating solution opposite the anode. The control section includes a regulating tank for regulating the composition and/or concentration of the plating solution, and a replenishing tank for injecting solution into the plating solution in the regulating tank. The plating apparatus also includes a mechanism for circulating plating solution between the regulating tank in the control section and the plating bath in the plating section. The plating section is installed in a first room, while the control section is installed in a second room, which is separate from the first room Accordingly, contamination in the plating section is prevented.

58 Claims, 10 Drawing Sheets



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6	US 6379520 B1	21				☑					USPAT
7	US 5906725 A	6				☑					USPAT

US-PAT-NO: 6458262

DOCUMENT-IDENTIFIER: US 6458262 B1

TITLE: Electroplating chemistry on-line monitoring and control system

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Brief Summary Text - BSTX (6):

High-pressure liquid chromatography (HPLC) has been proposed as a method to monitor plating bath constituents by Taylor et al. "Electroplating Bath Control for Copper Interconnects," Solid State Technology, vol. 4, issue Nov. 11, 1998. In this article, the authors describe using HPLC to separate electrolyte species. Although HPLC techniques have improved dramatically over the past decade, this type of analysis has limitations with regard to plating bath composition. While organic additives such as accelerators, suppressors, and levelers are well suited for chromatographic separation, some important primary bath species, ions, metal salts, and acids are not. Analysis of purified bath components via chromatography can provide valuable information about organic plating bath electrolyte components, but only provides a partial picture of the plating environment.

Current US Original Classification - CCOR (1):

205/82

(12) **United States Patent**
Reid

(10) **Patent No.: US 6,458,262 B1**
(45) **Date of Patent: Oct. 1, 2002**

(54) **ELECTROPLATING CHEMISTRY ON-LINE MONITORING AND CONTROL SYSTEM**

(75) Inventor: **Jonathan David Reid**, Sherwood, OR (US)

(73) Assignee: **Novellus Systems, Inc.**, San Jose, CA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 53 days.

(21) Appl. No.: **09/802,490**

(22) Filed: **Mar. 9, 2001**

(51) **Int. Cl.**[7] **C25D 21/14**

(52) **U.S. Cl.** **205/82**; 204/228.6; 204/229.2; 204/232; 204/237; 205/101

(58) **Field of Search** ..... 205/82, 99, 101; 204/228.1, 228.6, 229.2, 232, 237, DIG. 13

(56) **References Cited**

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Taylor, et al, "Electroplating bath control for copper interconnects", Solid State Technology, Nov. 1998, pp. 47–57.

Wikiel, et al., "On-Line Monitoring of Chemical Processes in Electronic Components Manufacturing", Technic, Inc., pp. 1–8. Date of Publication Not Available.

Paar, Anton, "L-DENS-Liquid Density Transmitter for OEM Applications (Original Equipment Manufacturer)", Instruction Book, Mar. 12, 1996, pp. 1–30.

"Quali-Line™ AC-1000", ECI Technology, 1993, pp. 1–2.

Bratin, Peter, "New Development in the Use of Cyclic Voltammetric Stripping for Analysis of Plating Solutions", pp. N1–N28. (Date of Publication Not Available).

"Real Time Analyzer (RTA) Technical Manual", Technic, of Providence, Rhode Island, pp. 1–19. Date of Publication Not Available.

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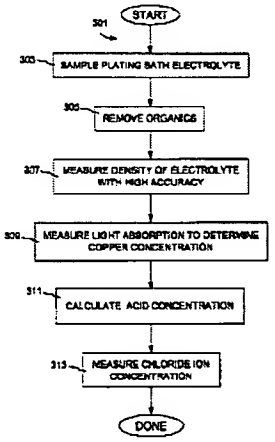
Primary Examiner—Nam Nguyen
Assistant Examiner—William T. Leader
(74) *Attorney, Agent, or Firm*—Beyer Weaver & Thomas, LLP

(57) **ABSTRACT**

The present invention provides methods and apparatus for analysis and monitoring of electrolyte bath composition. Based on analysis results, the invention controls electrolyte bath composition and plating hardware. Thus, the invention provides control of electroplating processes based on plating bath composition data. The invention accomplishes this by incorporating accurate bath component analysis data into a feedback control mechanism for electroplating. Bath electrolyte is treated and analyzed in a flow-through system in order to identify plating bath component concentrations and based on the results, the plating bath formulation and plating process are controlled.

36 Claims, 5 Drawing Sheets



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6	US 6379520 B1	21							☑				USPAT
7	US 5906725 A	6							☑				USPAT
8	US 5888373 A	5							☑				USPAT
9	US 5368715 A	15							☑				USPAT
10	US 5223118 A	15							☑				USPAT

US-PAT-NO: 5223118

DOCUMENT-IDENTIFIER: US 5223118 A

TITLE: Method for analyzing organic additives in an electroplating bath

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Abstract Text - ABTX (1):
A direct method of analyzing brighteners and levelers used in metal electroplating baths. The method is based on the differential adsorption of these additives on a working electrode during a sequence of steps prior to and during metal plating. The sensitivity of the method allows for the determination of both brightener and leveler in the same sample without cyclic processing.

Brief Summary Text - BSTX (5):
Electroplating is a complex process involving multiple ingredients in a plating bath. It is important that the concentration of several of the ingredients be kept within close tolerances in order to obtain a high quality deposit. In some cases, chemical analysis of individual solution constituents can be made regularly (such as pH measurement for acid content), and additions made as required. However, other addition agents such as brighteners, leveling agents, suppressants, etc., together with impurities, cannot be individually analyzed on an economical or timely basis by a commercial plating shop. Their operating concentration is low and their quantitative analysis is complicated and subject to error.

Brief Summary Text - BSTX (8):
The electroplating of through-hole interconnections in the manufacture of multilayer printed circuit boards is an example of the use of an electroplating metal where high quality plating is required. It is known that the concentration of the organic additives, such as brighteners and levelers, within the plating solution must be maintained in low concentration (typically less than 100 parts per million parts of solution - ppm) in order to obtain acceptable deposits on printed circuit boards. This must be done to maintain proper mechanical properties for resistance to thermal stresses encountered during manufacture and use and to assure the proper thickness of the deposit in the through-holes and leveling. The concentration of the organic additive agents fluctuates because of oxidation at the anode, reduction at the cathode, and chemical degradation. When the additive level is insufficient, deposits are burned and powdery in appearance whereas excessive addition agents induce brittleness and non-uniform deposition. Hull cell tests, Bone Pattern tests, and Pencil tests, combined with periodic additions of fresh additives, were the methods used to maintain a control concentration of the additive until recently. These methods were unreliable and circuit board quality suffered as a consequence of these unreliable methods.

Brief Summary Text - BSTX (9):
A more recent method for evaluating the quality of an electroplating bath was disclosed in Tench U.S. Pat. No. 4,132,605 (hereafter the Tench patent).

US005223118A

United States Patent [19]

Sonnenberg et al.

[11] **Patent Number: 5,223,118**

[45] **Date of Patent: Jun. 29, 1993**

[54] **METHOD FOR ANALYZING ORGANIC ADDITIVES IN AN ELECTROPLATING BATH**

[75] Inventors: Wade Sonnenberg, Foxboro; Roger Bernards, Wellesley; Patrick Houle, Framingham; Gordon Fisher, Sudbury, all of Mass.

[73] Assignee: Shipley Company Inc., Newton, Mass.

[21] Appl. No.: 666,798

[22] Filed: Mar. 8, 1991

[51] Int. Cl.[5] G01N 27/416; C25D 21/14

[52] U.S. Cl. 205/81; 204/153.1; 427/10

[58] Field of Search 205/81; 204/153.1, 434; 427/8, 10

[56] **References Cited**

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4,725,339	2/1988	Bindra	204/153.1
4,897,165	1/1990	Bernards et al.	204/24
4,917,774	4/1990	Fisher	204/153.1

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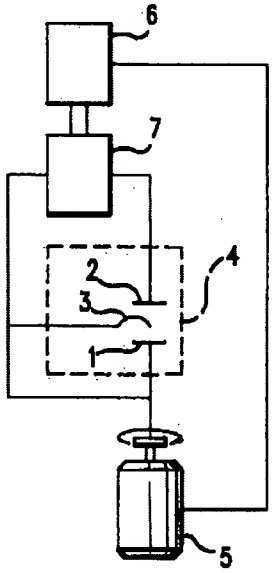
Tench et al., Pulse Voltammetric Stripping Analysis of Acid Copper Plating Baths, *J. Electrochem. Soc.*, Apr. 1985, pp. 831-834.

Primary Examiner—John Niebling
Assistant Examiner—William T. Leader
Attorney, Agent, or Firm—Robert L. Goldberg

[57] **ABSTRACT**

A direct method of analyzing brighteners and levelers used in metal electroplating baths. The method is based on the differential adsorption of these additives on a working electrode during a sequence of steps prior to and during metal plating. The sensitivity of the method allows for the determination of both brightener and leveler in the same sample without cyclic processing.

19 Claims, 9 Drawing Sheets